

SILICON CARBIDES WITH THE WURTZITE STRUCTURE

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In 1959, Adamsky and Merz [1] reported the synthesis and crystallographic properties of a silicon carbide with the wurtzite structure, $2H-SiC$. They prepared this carbide by thermal decomposition, in a hydrogen atmosphere, of methyltrichlorosilane or of a mixture of $SiCl_4$ and C_7H_8 , at 1400-1500°C. The crystals of $2H-SiC$ always grew on the sides or lid of the graphite crucible containing the gaseous reaction mixture. In all the specimens of $2H-SiC$ investigated, the presence of the cubic silicon carbide $\beta-SiC$ was noted, crystallographically intergrown with the large $2H-SiC$ crystals of forming globular masses on the ends of acicular $2H-SiC$ crystals.

No types of structure have been observed previously, in industrial silicon carbide, which had a numerical packing symbol including the number one. Mitchell [2] has expressed the opinion that two-layer packing in silicon carbide is an ideal structure which cannot exist in reality.

Since the discovery of Adamsky and Merz created a precedent, in that the $2H-SiC$ they obtained was prepared under specific conditions, it appeared of interest to note the possible formation of a wurtzite-type silicon carbide under different synthesis conditions.

We have detected $2H-SiC$ in the products obtained on synthesizing silicon nitride. The synthesis was carried out as follows. Powdered silicon (95% Si) was pressed with starch gum into a tablet, which was placed on a graphite support in the carbon tube of a Tammann furnace; here it was heated in a stream of nitrogen up to 1400°C, held at this temperature for 2 h, heated to 1600°C, and then held at 1600° for 2 h, after which the furnace was switched off and the specimen allowed to cool slowly in the furnace.

After the experiment was completed, a greenish, finely-dispersed deposit was noticed on the graphite support, a little distance away from the

tablet. The deposit was scraped off the support and investigated by x-ray diffraction. The tests were made in a powder camera with a working diameter of about 68 mm, in various radiations, i. e., copper, nickel, cobalt, iron, and chromium, both with the specimen-tube rotating and with it stationary. The x-ray tests showed that the deposit was a finely crystalline silicon carbide. Lines of other phases were not detected. The table shows the results obtained on indexing a powder photograph of the deposit taken in $Ni-K\alpha$ radiation. The reflection angles θ were determined allowing for absorption; the effective radius of the film was found from measurement of the asymmetric x-ray pattern.

From the distribution of the x-ray lines it could be assumed that this silicon carbide had a hexagonal structure, but with a lower number of packing layers, n_c , than in the common 6H and 4H silicon carbide structures. We therefore assumed that in the present case, $n_c = 2$. The indexing was done on the basis of the tetragonal arrangement, for hexagonal structures built up on the close-packed spheres principle, similar to the method used in [3, 4]. Initially we assumed that $a = 3.081$ Å, but later we determined the unit cell constants of the carbide under study more accurately, giving $a = 3.079$ Å; $c = 5.028$ Å; using these, the values of d_{calc} were corrected (see table).

The agreement between d_{exp} and d_{calc} was satisfactory for all the lines; the greatest discrepancy did not exceed ± 0.005 Å for $\theta < 50^\circ$ and ± 0.002 Å for $\theta > 50^\circ$. The agreement of d_{exp} with results in [1] was also completely satisfactory.

It should be noted that there were no signs of splitting in the reflections from the (006) and (302) planes; thus in the present case we observe the theoretical axial ratio of $c/a = 1.633$, in contrast to the result obtained in [1] of $c/a = 1.641$, for the

TABLE 1. Indexing the Powder Photograph of the Deposit Ni - K α Radiation

I_{exp} rel. (MF-4)	θ°	d_{exp} (kX)	2H - SiC		β - SiC		Results from [1] in Cu K α radiation	
			d_{calc}^* (kX)	hkl	d_{calc}^{**} (kX)	HKL	d_{exp} Å	I_{exp}
59.6	18.08 ₅	2.66 ₇	2.662	100			2.67	6.207
100	19.21 ₈	2.51 ₅	2.510	002	2.515	111	2.52	12.178
57.9	20.60 ₃	2.35 ₃	2.351	101			2.36	8.012
10.3	22.32 ₃	2.17 ₉			2.178	200	2.18	
11.2	23.96 ₁	1.82 ₆	1.826	102			1.83	2.877
88.5	32.57 ₄	1.538	1.538	110	1.540	220	1.54	
28.3	35.73 ₅	1.418	1.416	103			1.43	5.866
3.6	38.46 ₈	1.331	1.330	200			1.33	1.554
77.5	39.27 ₈	1.308	1.310	112	1.313	311	1.31	
20.2	40.09 ₁	1.286	1.287	201			1.29	2.588
10.8	41.16 ₀	1.258	1.255	004	1.258	222	1.26	2.531
2.6	44.57 ₇	1.180	1.176	202			1.18	0.842
1.7	46.67 ₀	1.138	1.135	104			—	0.613
5.6	49.66 ₀	1.086			1.089	400	1.09	
14.5	52.56 ₉	1.043	1.042	203			1.04	3.788
19.2	55.46 ₉	1.005	1.006	210				
21.7	56.23 ₉	0.995 ₈			0.999	331	1.01	
25.5	57.26 ₄	0.984 ₂	0.9865	211			0.987	
27.3	58.24 ₅	0.973 ₃	0.9719	114	0.974	420	0.975	
10.0	61.44 ₆	0.942 ₅	0.9392	105			0.947	3.779
6.5	62.47 ₂	0.933 ₆	0.9333	212			0.935	
1.3	64.86 ₁	0.914 ₅	0.9130	204			—	0.587
46.0	68.89 ₃	0.886 ₇	0.8871	300	0.889	422	0.890	5.225
26.5	73.52 ₁	0.862 ₆	0.8622	213			0.866	
v.w., diff.	80.42 ₃	0.838 ₉			0.8383	511; 333		
58,0	$\left\{ \begin{array}{l} \alpha_1 = 81.51_0 \\ \alpha_2 = 82.59_5 \end{array} \right\}$	0.836 ₃	0.8363	006; } 302 }			0.838	4.216+4.344

* Calculated for $a = 3.073$ kX.

** Calculated for $a_{\text{cub}} = 4.356$ kX, corresponding to $a = 3.080$ kX in the hexagonal arrangement.

same value of a . Calculation of the position of the 006 reflection using the data of [1] gives $\theta_{\alpha_{1006}} = 79.82^\circ$, which is far outside the limits of error of our measurements.

From the table it can be seen that there were only three lines which could not be assigned to the 2H-SiC structure, and these turned out to be the 200, 400, and 331 lines of cubic silicon carbide. The fact that the 511 + 333 lines of β -SiC did not coincide with the 006 + 302 lines of 2H-SiC, at the large reflection angles of $\theta \sim 80-82^\circ$, indicated that there was a difference between the a_{hex} values of the lattices of the two polytypes. In fact, for β -SiC, from $d_{\text{exp}511} = 0.8385$ Å a value of $a_{\text{cub}} = 4.359$ Å was found, equivalent in the hexagonal arrangement to $a_{\text{hex}} = 3.083$ Å. The remaining β -SiC lines fell on top of 2H-SiC lines.

Figure 1 shows powder photographs of 2H-SiC (a) and the common hexagonal structures 4H-SiC (b) and 6H-SiC (SiCII) (c), together with the cubic silicon carbide β -SiC (d).

The relative intensities of the lines on the powder photograph of the deposit were determined using a MF-4 microphotometer, with a logarithmic scale of peak heights. The resulting blackening

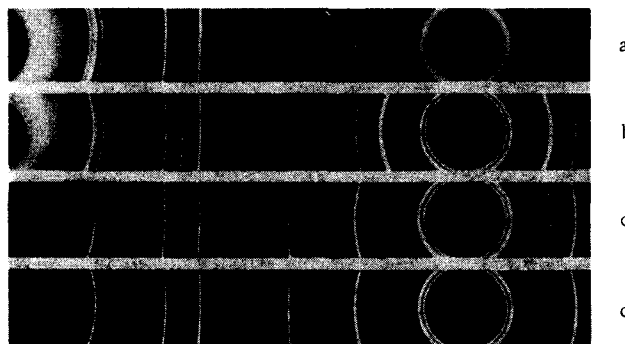


Fig. 1. Powder photographs of different silicon carbide structures. a) The two-layer hexagonal wurtzite-type structure 2H-SiC; b) the four-layer hexagonal wurtzite-type structure (SiCIII)-4H-SiC; c) the six-layer hexagonal wurtzite-type structure (SiCII)-6H-SiC; d) the three-layer cubic wurtzite-type structure (β -SiC)-3C-SiC. Filtered nickel radiation.

values were brought to a uniform scale on which the blackening of the strongest line, 2H-SiC-002, was taken as 100. Figure 2 shows graphically the values of the relative intensities of the lines on the powder photographs of the material under study, taken in copper, nickel, and cobalt filtered radia-

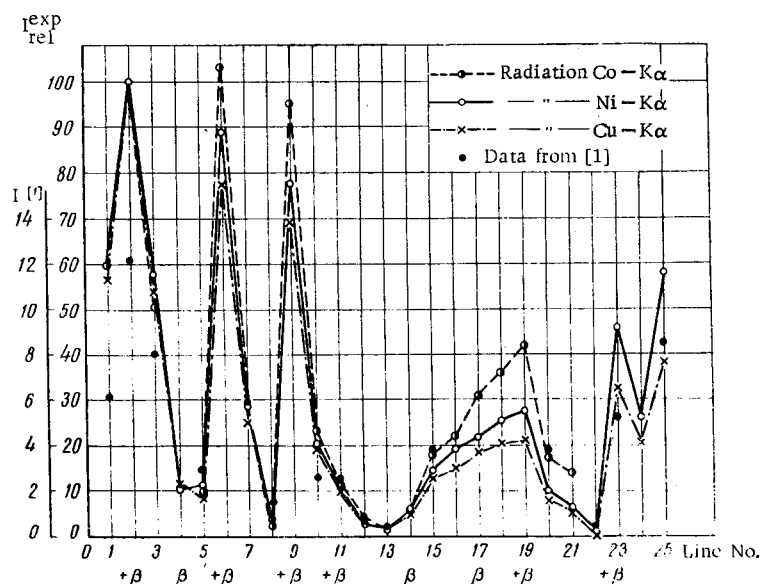


Fig. 2. Relative intensities of lines on the powder photographs of 2H-SiC.

tions. The table shows the numerical values of I_{rel} on the photograph taken in nickel radiation.

The values found for I_{rel} were only approximate estimates of the intensities of the 2H-SiC lines, since the cubic carbide present in the specimen gave lines which superimposed on those of 2H-SiC, and there was not a linear relationship between blackening and intensity for all the lines on the photographs. Nevertheless, there was good agreement between our results and those obtained by Adamsky and Merz for a 2H-SiC single crystal, for all reflections except the first two, which in [1] had lower intensities (see Fig. 2).

A qualitative spectrographic analysis of the deposit showed that its emission spectrum was similar to that of industrial silicon carbide, contaminated with calcium, aluminum, and iron.¹ After washing some of the experimental powdered material in hydrofluoric acid, it became richer in the wurtzite form of silicon carbide, because the finer particles of cubic carbide went out with the filtrate. A more careful analysis was not carried out because of the meager amount of material available.

Thus a rare wurtzite-type silicon carbide polype 2H-SiC, similar to that reported by Adamsky and Merz, was obtained in the same temperature range, 1400-1600°C, but under completely different conditions, i.e., in an atmosphere of nitrogen from the solid reactants silicon and graphite [5]. The silicon carbide synthesis took place through the reaction of a gaseous siliciding agent and solid carbon.

The role of the nitrogen in our experiment needs to be explained. It appears that the nitrogen must have brought about a sufficient partial pressure of the gaseous silicon-containing component for the formation of 2H-SiC to take place.

It should be emphasized that the wurtzite-type silicon carbide was found on the graphite support away from the silicon tablet; at the point where the silicon tablet was in direct contact with the graphite support, i.e., where direct access was restricted, β = SiC was formed.

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¹The analysis was carried out in the spectrographic laboratory of our institute, under the direction of the laboratory head, R. L. Pevsner.